

ENVIRONMENTAL ANALYSIS

UPTAKE OF DIVALENT METAL IONS (Cu^{2+} , Ni^{2+} , AND Co^{2+}) BY POLYSILOXANE IMMOBILIZED TRIAMINE-THIOL AND THIOL-ACETATE LIGAND SYSTEM

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ABSTRACT

Insoluble porous solid polysiloxanes-immobilized ligand systems bearing hybrid mixture of triamine-thiol ligand and thiol-acetate ligand as chelating functional groups of the general formula $\text{P}-(\text{CH}_2)_3-\text{X}(\text{Y})$ (Where P represents a silica like siloxane framework and X represents a mixture of triamine and thiol, $-\text{NHCH}_2)_2\text{NH}-(\text{CH}_2)_2-\text{NH}_2$ and $-\text{SH}$, and Y represents a thiol-acetate $-\text{SCH}_2\text{COOH}$ functional groups) has been prepared. The immobilized triamine-thiol ligand system was prepared through the sol-gel process by hydrolytic

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polycondensation of $\text{Si}(\text{OEt})_4$ and a mixture of 3-mercaptopropyltrimethoxysilane and 3-diethylenetriaminepropyltrimethoxysilane coupling agents. The immobilized thiol-acetate ligand system was prepared by the reaction of polysiloxane immobilized thiol ligand with ethylchloroacetate. These ligand systems exhibit high potential for extraction and preconcentration of divalent metal ions (Co^{2+} , Ni^{2+} and Cu^{2+}). The results indicate that the triamine-thiol ligand seems to form 1:1 metal to ligand complexes, where there is no clear stoichiometry structure in the case of the thiol-acetate ligand.

Key Words: Metal uptake; Triamine-thiol ligands; Thiol-acetate ligands polysiloxanes; Immobilized-polysiloxane ligand systems

INTRODUCTION

Several chelating functional groups have been incorporated within the polysiloxane cross-linking framework including amines, thiols, phosphines, glycinate, iminodiacetate and macrocyclic derivatives (1–8). The polysiloxane immobilized ligand systems were prepared by the sol-gel process based on hydrolytic polycondensation of tetraethylorthosilicate (TEOS) and the appropriate silane coupling agent of formula $(\text{RO})_3\text{Si-Z}$ where R represents methoxy or ethoxy hydrolysable group and Z is an organofunctional group. These polysiloxane ligand systems have great potential in the preconcentration, extraction and separation of metal ions from aqueous solutions (1,2,7,8), as a heterogeneous catalysis (3) and as stationary phases in chromatography (9). The polysiloxane immobilized ligand systems show high degrees of thermal and mechanical stability over the traditional organic polymers (10,11). The structural properties of these materials have been recently investigated using high resolution solid-state nuclear magnetic resonance (NMR) techniques and other chemical tools (12–20). Despite the fact that the immobilized amine ligands are of great importance because of its applications, they suffer from substantial degradation in acid solutions (7,21). In this study, hybrid mixtures of immobilized triamine-thiol and thiol-acetate were prepared to examine their stability and selectivity properties towards some divalent metal ions from aqueous solutions.

EXPERIMENTAL

Reagents and Materials

Tetraethylorthosilicate, 3-diethylenetriaminepropyltrimethoxysilane, 3-mercaptopropyltrimethoxysilane and ethylchloroacetate, were purchased from (MERCK) and used as received. Diethyl ether and absolute methanol (reagent grade) were used as received. Metal(II) solutions of the appropriate concentration were prepared by dissolving the metal(II) chloride (analar grade) in deionized water. Different pH ranges were prepared. Acetate solutions were prepared using hydrochloric acid/sodium acetate for pH (1–3), acetic acid/sodium acetate buffer for pH (4–6) and acetic acid/NaOH solutions for pH 6.5–8.

General Techniques

Analysis for carbon, hydrogen, and nitrogen were carried out, using an Elemental Analyzer EA 1110-CHNS CE Instrument. The concentrations of metal ions in their aqueous solutions were measured using a Perkin-Elmer Analyst-100, spectrometer. The infrared spectra for the materials were recorded on a SHIMADZU FTIR - 8201PC, spectrometer using KBr disk in the range 4000 to 400 cm^{-1} . All pH measurements were obtained using WTW 521 pH Meter. All ligand samples were shaken in aqueous metal ion solutions using ELEIA MMS Multi zzzShaker.

Methods of Preparation

Preparation of Polysiloxane-Immobilized Triamine-Thiol Ligand System (PTS)

This polysiloxane-immobilized ligand system was prepared by dissolving tetraethylorthosilicate (20.83 g, 0.10 mol) in 30 cm^3 methanol and 6.3 cm^3 HCl, 0.42 M. The mixture was stirred for few minutes. 3-Mercaptopropyltrimethoxysilane (9.82 g, 0.05) was added followed by 3-diethylenetriaminepropyltrimethoxysilane (13.27 g, 0.05 mol). Gelation occurred within 15 min, the product was then left to stand at RT for 12 h then dried in a vacuum oven at 90°C. The product was crushed, sieved, washed with successive portions, 50 cm^3 , of 0.025 M NaOH, water,

methanol and diethyl ether. The product was dried in a vacuum oven (0.1 torr) at 90°C for 10 h.

Preparation of Polysiloxane-Immobilized Thiol Ligand System (PS)

The thiol polysiloxane was prepared as previously described (12) by reaction of tetraethylorthosilicate with 3-mercaptopropyltrimethoxysilane in the presence of HCl.

Preparation of Polysiloxane-Immobilized Thiol-Acetate Ligand System (PSA)

5.0 g of polysiloxane thiol ligand system (PS) was refluxed for 72 hours with an excess of ethylchloroacetate (50 cm³) in a round bottom flask, in the presence of few drops of triethylamine. The solid product was filtered off, washed with successive portions, 50 cm³, of 0.025 M NaOH, water, methanol and diethyl ether. The product was dried in a vacuum oven (0.1 torr) at 90°C for 12 h.

Hydrolysis of Thiol-Acetate Ligand System (PSAH)

A 5.0 g of thiol-acetate polysiloxane ligand system (PSA) was refluxed with 150 cm³ of 2.0 M HCl for 10 hours. The solid material was filtered, washed with successive portions, 50 cm³, of 0.025 M NaOH, water, methanol and diethyl ether. The product was dried in vacuum (0.1 torr) at 100°C for 10 h.

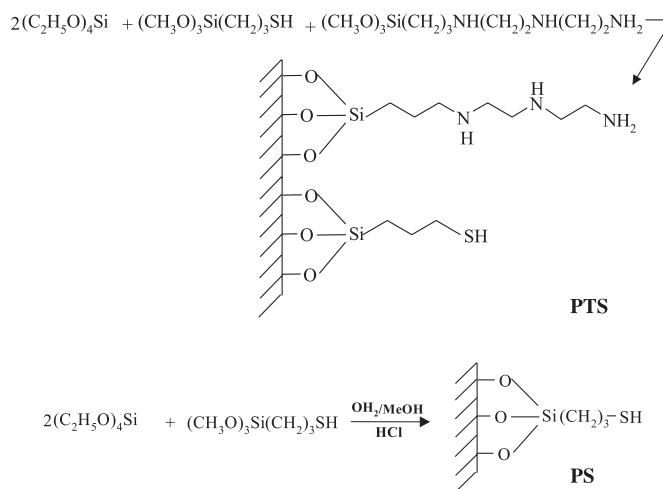
Metal Uptake Experiments

A 250 mg of each functionalized polysiloxane-immobilized ligand system was shaken with 50 cm³, 0.02 M of an aqueous solution of the appropriate metal(II) ions (Cu²⁺, Ni²⁺ and Co²⁺) using 250-cm³ polyethylene bottles. Measurement of the metal ion concentration was carried out by allowing the insoluble complex to settle down and appropriate volume of the supernatant was withdrawn using a micropipette then diluted to the linear range of the calibration curve for each metal. The metal ion uptake was calculated as mmol of M²⁺/g ligand.

RESULTS AND DISCUSSION

Preparation of Polysiloxane-Immobilized Thiol and Triamine-Thiol Ligand Systems (PTS & PS)

The mercaptopropyltrimethoxysilane or polysiloxane systems (PS) and PTS were prepared by mixing TEOS with mercaptotrimethoxysilane or with a mixture of 3-diethylenetriaminepropyltrimethoxysilane and 3-mercaptopropyltrimethoxysilane respectively (Scheme 1).



Scheme 1.

The elemental analysis along with the expected results are given in Table 1.

The elemental analysis given in Table 1 indicate that the found percentages are lower than the expected ones. This is due to the formation of small oligomers, which are water soluble. The formation of these oligomers is due to different rate of hydrolysis and incomplete hydrolytic polycondensation of the different reactants (1,6,7,14).

Preparation of Thiol-Acetate Ligand System (PSA)

The thiol-acetate immobilized ligand system (PSA) was prepared in a similar procedure used for the glycinate ligand system (8) by the reaction of

Table 1. Elemental Analysis Data for Polysiloxane-Immobilized Thiol (PS) and Thiol-Acetate (PSA) Ligand and Its Hydrolyzed (PSAH) System

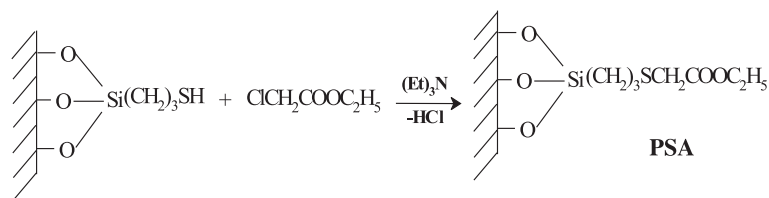
Type	Element	C%	H%	N%	S%	C/S	mmol S/g
PTS	Expected*	27.1	5.6	9.5	7.2	1.0	2.3
	Found	22.3	4.2	7.8	6.1	1.0	1.9
PS	Expected*	14.6	2.8	–	13.0	3.0	4.0
	Found	10.3	3.2	–	10.4	2.6	3.3
PSA	Expected ^a	21.4	3.3	–	8.14	7.0	2.7
	Found	15.7	3.7	–	6.7	6.2	2.1
PSAH	Expected ^b	11.9	2.5	–	7.1	4.4	2.1
	Found	13.0	3.5	–	7.2	4.9	2.3

*The expected values were calculated on the basis of the stoichiometry of the reactants, and complete hydrolysis and polycondensation of reactants.

^aThe expected values were calculated based on the found values of the thiol PS ligand system.

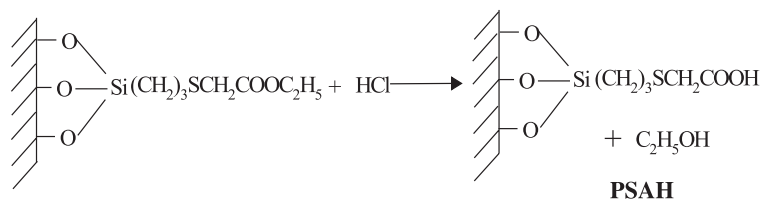
^bThe expected values were calculated based on the found values of the unhydrolyzed ligand system.

polysiloxane-immobilized thiol ligand system (PS) with an excess of ethylchloroacetate in the presence of triethylamine to facilitate the removal of generated HCl, (Scheme 2). The microanalysis data for the resulting product along with the expected values are summarized in Table 1.

**Scheme 2.**

From the results given in Table 1 it is possible to suggest that the reaction between 3-mercaptopropylpolysiloxane and ethylchloroacetate is evident from the increase of carbon and decrease of sulfur percentages in the resulting polysiloxane, compared with the thiol polysiloxane system (PS).

The PSA ligand system was hydrolyzed by an aqueous solution of 2 M HCl (Scheme 3). The elemental analysis data for this functionalized ligand along with the expected values are given in Table 1. The decrease of the



Scheme 3.

calculated C and S percentages are evident for the hydrolysis of ethoxy groups upon treatment with HCl. The slightly higher C percentage than the expected value are due to the presence of some unhydrolyzed ethoxy groups.

The FTIR spectra for thiol (PS), thiol-acetate (PSA) and its hydrolyzed form (PSAH) polysiloxane ligand systems are obtained. Three characteristic regions at $3000\text{--}3500\text{ cm}^{-1}$, $1500\text{--}1750\text{ cm}^{-1}$ and $900\text{--}1200\text{ cm}^{-1}$, are identified corresponding to $\nu(\text{OH})$, $\nu(\text{C}=\text{O})$ and $\nu(\text{SiO})$ vibrations. These assignments were based on literature spectral data reported for similar systems (24–26). The IR spectrum for thiol-acetate polysiloxane ligand (PSA) shows an absorbance band at 1718 cm^{-1} due to ester $\nu(\text{C}=\text{O})$ stretching vibration. This band was not found in the IR spectrum of 3-mercaptopropylpolysiloxane. The IR spectrum for the hydrolyzed ligand system (PSAH) shows two bands at 1726 cm^{-1} and 1643 cm^{-1} which are assigned to $\nu(\text{C}=\text{O})$ acid form and $\delta(\text{O-H})$ vibrations.

Proton Uptake

The proton uptake ($\text{mmol H}^+/\text{g}$ ligand) was studied for the polysiloxane-immobilized triamine-thiol (PTS) ligand system. The results of the uptake versus time along with that of the nitrogen obtained from the elemental analysis are given in Table 2.

Table 2. Proton Uptake Capacity of (PTS)

Ligand system	mmol H^+ per gram of the ligand							mmol N/g ligand
	1 h	2 h	5 h	10 h	24 h	48 h	72 h	
PTS	3.40	3.82	6.86	9.10	9.52	9.52	9.52	5.6

It is obvious from Table 2 that the proton uptake capacity increases with time and reaches a maximum after 24 h. It is found that the maximum proton uptake (9.52) exceeds the value obtained from the elemental analysis (5.6), which reflects the interaction of HCl with the siloxane network (7).

Metal Uptake

The metal ion uptake capacity (Cu^{2+} , Ni^{2+} and Co^{2+}) as $\text{mmol M}^{2+}/\text{g}$ ligand, was determined by shaking the functionalized ligand systems (PTS) and (PSAH) in aqueous solution of the divalent metal ions at different time intervals. The results are given in Figures 1–6. It is shown that the metal ion uptake is increased as a function of exposure time and reached an equilibrium, where maximum uptake is obtained. In a contrast to the immobilized triamine ligand system (27), in which the metal uptake capacity decreases after reaching its maximum, the triamine-thiol system exhibit almost no decreasing of metal uptake capacities (Figures 1–3). This is probably due to the presence of the thiol group (SH) as a diluent functional group which perhaps stabilize the ligand system. The metal chelate complexes of the triamine-thiol (PTS) and thio-acetate ligand systems are expected to form 1:1 or 2:1 ligand to metal complexes. From the elemental analysis of PTS

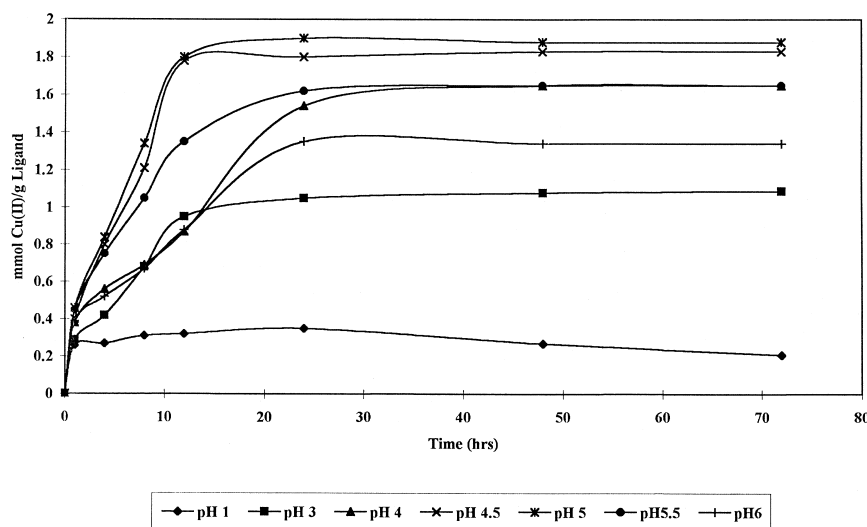


Figure 1. The uptake of Cu^{2+} ions by polysiloxane immobilized triamine-thiol (PTS) ligand system versus time at different pH (1–7, HCl/acetate solutions).

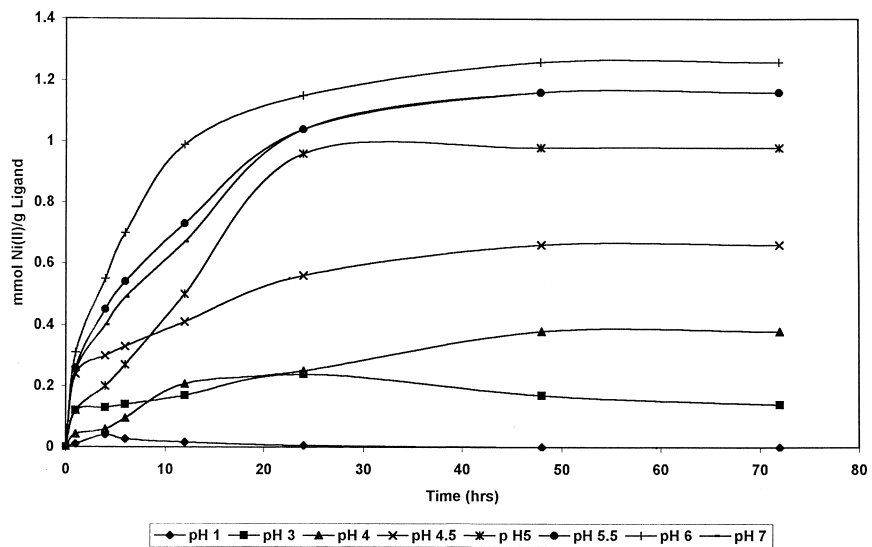


Figure 2. The uptake of Ni²⁺ ions by polysiloxane immobilized triamine-thiol (PTS) ligand system versus time at different pH (1–7, HCl/acetate solutions).

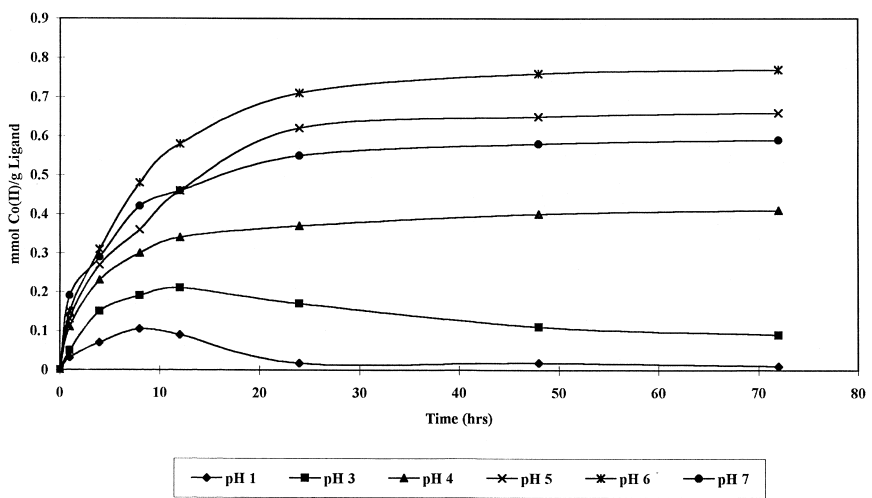


Figure 3. The uptake of Co²⁺ ions by polysiloxane immobilized triamine-thiol (PTS) ligand system versus time at different pH (1–7, HCl/acetate solutions).

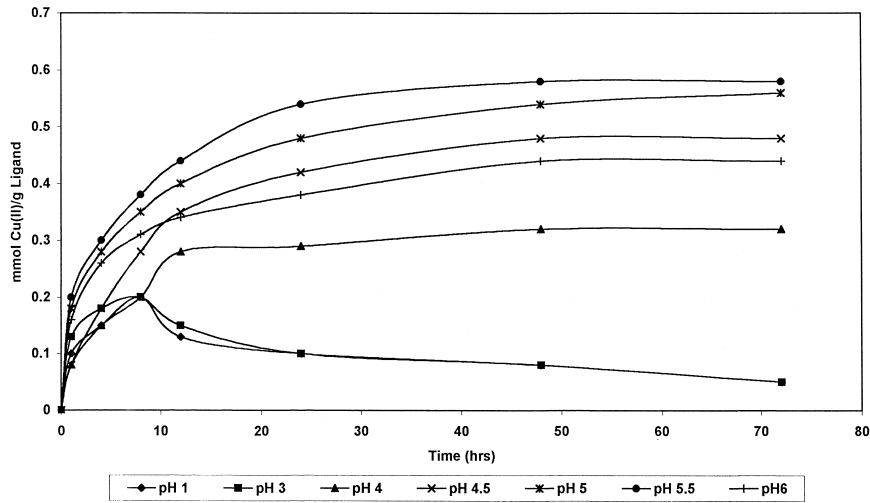


Figure 4. The uptake of Cu^{2+} ions by polysiloxane immobilized thiol-acetate (PSA) ligand system versus time at different pH (1–7, HCl/acetate solutions).

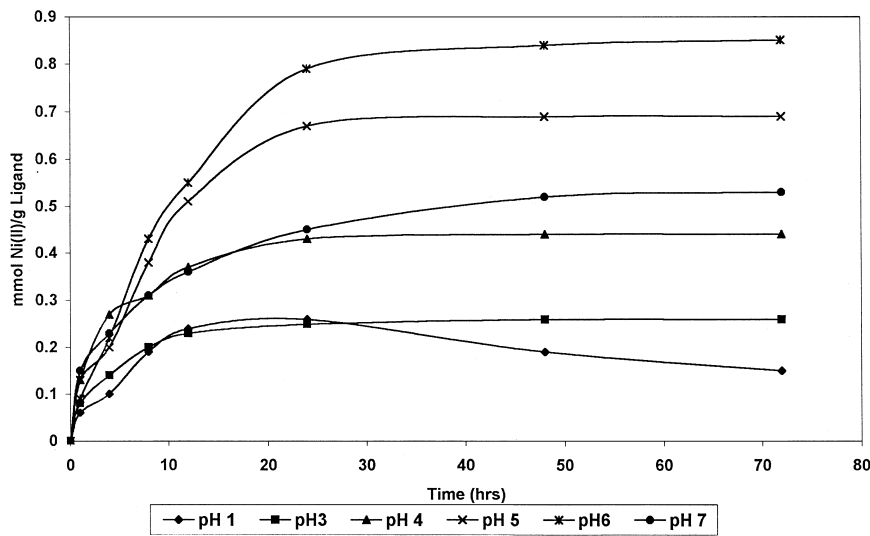


Figure 5. The uptake of Ni^{2+} ions by polysiloxane immobilized thiol-acetate (PSA) ligand system versus time at different pH (1–7, HCl/acetate solutions).

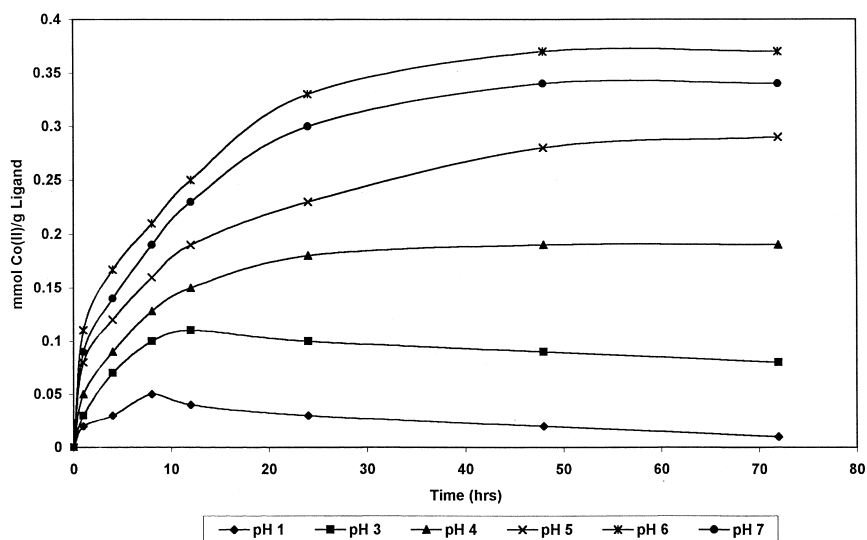


Figure 6. The uptake of Co^{2+} ions by polysiloxane immobilized thiol-acetate (PSA) ligand system versus time at different pH (1–7, HCl/acetate solutions).

which contains (6.5 mmol N/ligand) and the maximum uptake of copper (1.9 mmol Cu^{2+} /g ligand), it is possible to suggest that 1: ligand to metal complex is formed. In the case of thiol-acetate ligand, the metal to ligand is far from any expected stoichiometry. This is probably due to that the hydrolysis of the ethyl acetate groups are incomplete which was confirmed from the elemental analysis results. Another reason for this is perhaps the irregularity of the ligand groups on the ligand matrix so not all ligand sites are available for coordination to the metal ions, so it is therefore difficult to suggest a stoichiometry structure for the complex.

Effect of pH

The effect of the pH value on the uptake of Cu^{2+} , Ni^{2+} and Co^{2+} ions by PTS and PSAH is shown in Figures 7–8. The results show an increase of metal ion uptake with increasing pH value and reached its maximum at pH 5 in case of copper and at pH 6 in the case of nickel and cobalt. Only minor uptake capacity occurs at lower pH values (pH 1–3) due to the protonation of the amine moieties in the case of PTS and undissociated carboxylic

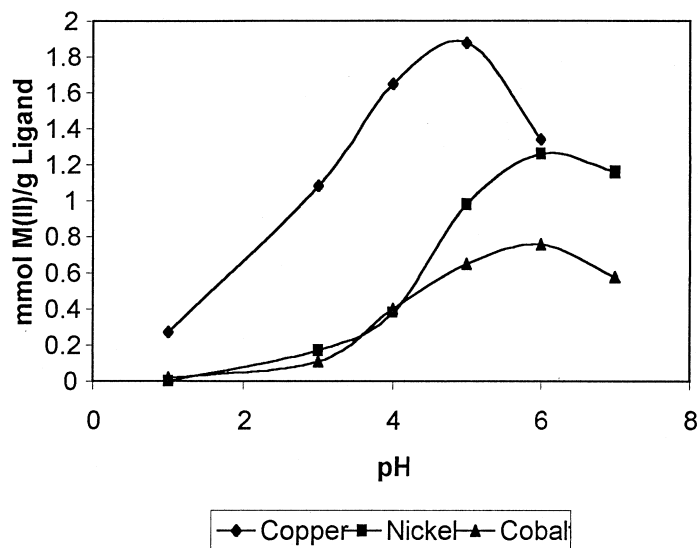


Figure 7. Uptake of Cu^{2+} , Ni^{2+} and Co^{2+} metal ions triamine-thiol ligand system versus pH (1-7, HCl/acetate solutions).

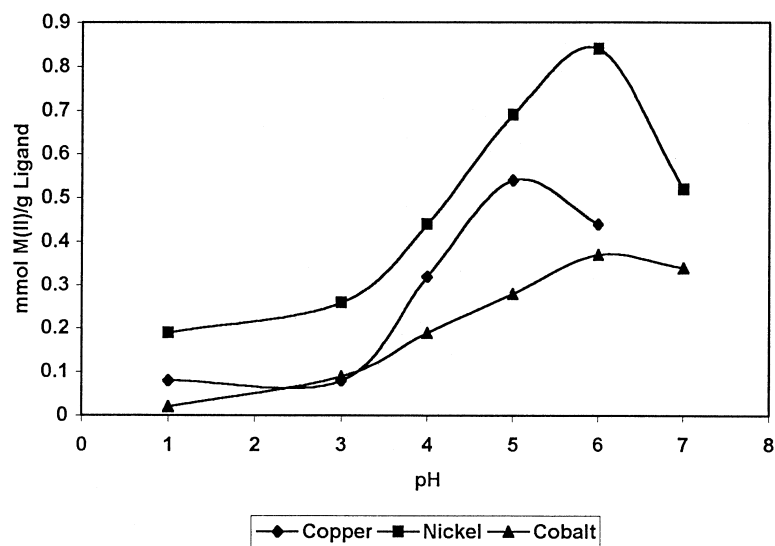


Figure 8. Uptake of Cu^{2+} , Ni^{2+} and Co^{2+} metal ions by thiol-acetate ligand system, versus pH (1-7, HCl/acetate solutions).

groups in the case of PSAH (7,8,28) and therefore reduces the ability of these groups to involve in chelate formation with metal ions. Metal ion uptake starts to decrease after the maximum value due to the formation of metal hydroxides (7,8,28,29).

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